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EXCITED-STATE ABSORPTION OF 4'-(5'''-R-PYRIMIDYL)-2,2':6',2''-TERPYRIDYL PLATINUM(II) PHENYLACETYLIDE COMPLEXES (PREPRINT)

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Excited-state absorption of 4'-(5'''-R-pyrimidyl)-2,2':6',2''-terpyridyl platinum(II) phenylacetylide complexes

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Abstract

The singlet excited-state absorption of five 4'-(5'''-R-pyrimidyl)-2,2':6',2''-terpyridyl platinum(II) phenylacetylide complexes were investigated using fs pump-probe UV-Vis spectroscopy. These complexes exhibit broad, moderately intense S_1 - S_n absorption from 500 to 800 nm, which could be attributed to the $^1\text{MLCT}$ state. The S_1 - S_n absorption band energy is influenced by the substituent on the 5'''-position of the pyrimidyl ring, with an electron-donating substituent increasing the energy, and electron-withdrawing substituent decreasing it. The singlet excited-state lifetime deduced from the decay of the fs transient absorption is in the range of 37 – 139 ps. Open-aperture Z-scan experiments using ns and ps lasers at 532 nm for **1-5** were carried out in CH_3CN solutions and the wavelength dispersion characteristics of **1** was investigated using ps laser at various wavelengths. Reverse saturable absorption (RSA) is observed for all complexes at 532 nm for both ns and ps Z scans, and RSA occurs at 500 – 600 nm for **1** for ps laser. Fitting of the experimental Z-scan data using a five-level dynamic model gives rise to the quantitative singlet and triplet excited-state absorption cross-sections, which varies from $(18 \pm 1) \times 10^{-18} \text{ cm}^2$ to $(50 \pm 5) \times 10^{-18} \text{ cm}^2$ for σ_s and $(11 \pm 1) \times 10^{-18} \text{ cm}^2$ to $(14 \pm 2) \times 10^{-18} \text{ cm}^2$ for σ_T at 532 nm, corresponding to a ratio of 6.5 – 29.8 for σ_s/σ_g and 2.8 – 11.2 for σ_T/σ_g for **1-5**. Complexes **1**, **2** and **4** exhibit a much larger σ_s/σ_g compared to those of **3** and **5**. Moreover, the σ_s/σ_g ratio increases from 1.9 at 500 nm to 260 at 600 nm for complex **1**.

Keywords: Excited-state absorption, ground-state absorption, cross-section, transient difference absorption, Z scan, platinum complex

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1. Introduction

Organic compounds with large and fast nonlinear absorption have attracted great interest in the past a few decades because of their potential applications in photonic devices [1], such as passive mode locking [2], optical switching [3,4], optical rectification [5], laser pulse shaping and stabilization [6,7], *etc.* The reverse saturable absorption of a variety of organic and organometallic compounds have been investigated and reported, which include porphyrins [8], phthalocyanines [9], naphthalocyanines [10], fullerenes [11], cyanines [12], and indanthrone derivatives [13]. Among these chromophores, phthalocyanines and naphthalocyanines have been revealed as one of the most promising reverse saturable absorbers due to their low ground-state absorption but high excited state absorption in the spectral region between the B band and Q band [9,10]. However, the dark green color of the phthalocyanines prevents their potential application as broadband reverse saturable absorbers.

In the past a couple of years, square-planar platinum complexes have drawn considerable interest as broadband nonlinear absorbing materials. Studies on a platinum:ethynyl complex by McKay and co-workers revealed that this complex exhibited weak ground-state absorption from 450 to 1100 nm, but strong reverse saturable and/or two-photon absorption in this spectral region [14-18]. Recent work by Cooper/Rebane/Schanze and co-workers reported that a series of platinum acetylide chromophores with π -donor or π -acceptor moieties showed strong two-photon absorption cross-sections in the region of 600-700 nm and 750-800 nm [19]. Glomsdal and co-workers also found that some thiophenyl Pt(II)-ethynyl derivatives had moderate two-photon absorption cross-section at the near-IR region [20]. These results are quite intriguing; however, these complexes are unstable upon laser irradiation due to the presence of trialkylphosphine ligands.

To overcome this disadvantage, our group becomes interested in square-planar platinum terdentate complexes [21,22]. Similar to that in the platinum acetylide complexes mentioned in the previous paragraph, the heavy-atom effect in these platinum terdentate complexes facilitates intersystem crossing and thus generally results in moderate to high triplet excited-state population, which would in turn enhance the triplet excited-state absorption. However, unlike the reported platinum acetylide complexes, the platinum terpyridyl or C^NN^N (C^NN^N represents 6-phenyl-2,2'-bipyridine) acetylide complexes typically possess multiple charge transfer states, such as metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), and/or intraligand charge transfer (ILCT) [21,22]. The presence of these charge transfer state could give rise to broadband singlet and triplet excited state absorption extending from near-UV to the near-IR region. More importantly, these platinum terdentate complexes exhibit excellent thermal and photochemical stability; therefore, they are more suitable for photonic device applications.

In the past six years, we have investigated several series of platinum terdentate complexes with different types of terdentate ligand, different substituents on the terdentate ligand, and different acetylide ligands [23-34]. Our study discovered that alternation of the terdentate ligand, the substituent on the terdentate ligand, and the substituent on the acetylide ligand influences the excited-state characteristics significantly. For example, our photophysical studies on five 4'-(5'''-R-pyrimidyl)-2,2':6',2''-terpyridyl platinum(II) phenylacetylide complexes (structure shown in Figure 1) demonstrated that because of the coplanarity of the pyrimidyl ring with the terpyridyl

ligand conjugation between the pyrimidyl ring and the terpyridyl ligand could occur [28]. Consequently, the electronic effect from the 5'''-substituent could influence the MLCT state energy, which is reflected by the lowest-energy absorption band energy, the emission band energy, and the triplet transient difference absorption band energy. In addition, the triplet excited-state absorption coefficient and quantum yield are affected by the 5'''-substituent as well. However, the effect of these substituents on the singlet excited-state absorption characteristics has not been investigated, and the quantitative singlet and triplet excited-state absorption cross-sections at various visible wavelengths have not been reported. To remedy these deficiencies, fs transient difference absorption spectra of these five 4'-(5'''-R-pyrimidyl)-2,2':6',2''-terpyridyl platinum(II) phenylacetylide complexes have been investigated; and the open aperture ps and ns Z scans were conducted at 532 nm for these five complexes. ps Z scans at different wavelengths for **1** were also carried out. Furthermore, these Z-scan data were fitted numerically using a five-level model to deduce the singlet and triplet excited-state absorption cross sections at each respective wavelength.

2. Experimental Section

The synthesis, characterization, UV-Vis absorption spectra, and triplet transient difference absorption spectra of complexes **1-5** were reported by our group previously [28]. The fs transient difference absorption was measured by a femtosecond pump-probe UV-vis spectrometer (HELIOS) manufactured by Ultrafast Systems LLC. The acetonitrile solution of the complex in a 2-mm cuvette was excited at 400 nm with a 240-fs pulse from a Ti:Sapphire laser (Clark-MXR CPA 2010, 1 kHz repetition rate, 1 mJ/pulse at 780 nm), and the absorption was probed from 425 to 800 nm with white-light continuum.

For open-aperture Z-scan measurement [35], the second harmonic output (532 nm) of a Q-switched Quantel Brilliant Nd:YAG laser with a pulsewidth of 4.1 ns and a repetition rate of 10 Hz was used as the light source for ns measurements; and an EKSPLA optical parametric generator (OPG) (PG 401) pumped by the third harmonic of a Nd:YAG laser (EKSPLA PL 2143A) with a pulse width of 27 ps and a repetition rate of 10 Hz was used for the ps Z-scan measurement. The spatial profile of both the ns and ps laser beams was nearly Gaussian distribution. The ns laser beam was focused by a $f = 30$ cm plano-convex lens and the radius of the beam waist was $\omega_0 = 28 \mu\text{m}$, corresponding to a Rayleigh length of 4.6 mm. This ensures that the sample in the 1-mm thick cuvette can be treated as a thin sample. For picosecond Z-scan experiments, the focal length of the plano-convex lens was 15 cm, resulting in a beam waist of $\omega_0 = 26 \mu\text{m}$ at 500 nm, $39 \mu\text{m}$ at 532 nm, $30 \mu\text{m}$ at 550 nm, and $29 \mu\text{m}$ at 570 and 600 nm. The corresponding Rayleigh length was 4.3 mm, 9.0 mm, 5.1 mm, 4.6 mm, 4.4 mm and 4.4 mm at 500 nm, 532nm, 550 nm, 570 nm and 600 nm, respectively. The pathlength of the cuvette used for the ps Z-scan measurement was 2 mm, which is obviously shorter than the Rayleigh length at each respective wavelength; therefore the sample can be treated as thin sample as well.

The open-aperture Z-scan results were fitted by a five-level dynamic model [27,36] that composed of a ground state (S_0), two singlet excited states (S_1 and S_2), and two triplet excited states (T_1 and T_n). The population at each state was tracked during the laser irradiation in this model. The ground-state absorption cross-section obtained from the UV-Vis absorption measurement, the singlet excited-state lifetime from the decay of the fs transient absorption measurement, and the triplet excited-state lifetime and quantum yield from the ns transient

absorption measurement were used as the input parameter to fit the ns and ps Z-scan data simultaneously. The set of the excited-state absorption cross-section (σ_s and σ_T) that best fits both the ns and ps experimental data is reported in this paper for each complex. The details of the rate equations and the fitting procedure were described in our previous publications [27,36].

3. Results and Discussion

In order to study the nonlinear absorption, the ground-state absorption characteristics need to be investigated to obtain the ground-state absorption cross-section and figure out the optical window for nonlinear absorption. The UV-Vis absorption spectra of **1-5** in CH₃CN have been reported by our group previously and a representative spectrum is provided in Figure 2. As exemplified by complex **4** in Figure 2, the UV-Vis absorption spectrum composes of intense absorption bands in the UV region, which is attributed to the $^1\pi,\pi^*$ transitions within the ligands, and broad, moderately strong charge transfer absorption that could admix metal-to-ligand charge transfer ($^1\text{MLCT}$) and ligand-to-ligand charge transfer ($^1\text{LLCT}$) between 380 nm and 580 nm. Above 550 nm, the complex is essentially transparent, which provides a broad optical window where reverse saturable absorption could occur. As reported earlier by our group, the energy of the charge transfer band is affected by the substituent at the 5'''-position of the pyrimidyl ring, and a linear correlation between the Hammett constant of the substituent and the absorption band energy was discovered [28]. Nevertheless, the ground-state absorption cross-section for each of these complexes at different wavelengths can be deduced from the molar extinction coefficients at each respective wavelength and the results are listed in Tables 2 and 3, respectively.

The triplet transient difference absorption spectra (TA) of **1-5** were measured using 4.1 ns laser excitation at 355 nm. The results were published previously [28] and the typical spectrum is exemplified in Figure 2 by **4** along with its ground-state absorption spectrum. The TA spectrum clearly shows a bleaching band in the 420 – 500 nm spectral region and a broad positive absorption band from 500 nm to 800 nm. Considering the coincidence of the bleaching band position with the $^1\text{MLCT}/^1\text{LLCT}$ band and the similar shape of the positive absorption band with other platinum terpyridyl acetylide complexes reported in the literature [37], the excited state that gives rise to the observed transient absorption spectrum is tentatively assigned to the $^3\text{MLCT}$ state. In line with the trend observed in the UV-Vis absorption [28], electron-withdrawing substituent (-CN) at the 5'''-position of the pyrimidyl ring causes a red-shift of the T_1 - T_n absorption band; while electron-donating substituent (-OEt) induces a blue-shift. The triplet lifetime deduced from the decay of the triplet transient absorption is in the range of 130 - 340 ns for **1-5**, and the quantum yield of the triplet excited-state formation is measured to be 0.19 - 0.66 for **1-5** by the comparative method using SiNc in benzene ($\Phi_T = 0.20$, $\epsilon = 70,000 \text{ M}^{-1}\text{cm}^{-1}$) [38] as the reference.

Similar to the ns transient difference absorption, the fs transient difference absorption of **1-5** also exhibits a bleaching band at the $^1\text{MLCT}/^1\text{LLCT}$ spectral region and broad singlet excited-state absorption from 500 to 800 nm, as exemplified by **1** in Figure 3. The S_1 - S_n absorption band maxima are listed in Table 1 for **1-5**. Similar to that observed in the UV-Vis absorption and triplet transient difference absorption spectra [28], the singlet excited-state absorption band maximum appears at a shorter wavelength (685 nm) for complex **2** that possesses the electron-donating substituent (-OEt); while the absorption band maximum occurs at 766 nm for complex **5** with electron-withdrawing -CN substituent on the 5'''-position of the pyrimidyl ring. This

provides another piece of evidence for electronic delocalization between the pyrimidyl ring and the terpyridyl component due to improved coplanarity.

However, unlike the ns transient absorption, the decay of the fs transient absorption for **1-5** appears to be complicated. The decay kinetics typically consists of a short (< 5 ps) decay that could be attributed to intramolecular vibrational relaxation from upper vibrational levels upon excitation, followed by an intermediate decay of tens 37 – 139 ps, which is assigned as the singlet excited-state lifetime due to the repopulation of the ground state and triplet excited state via fluorescence, internal conversion, and intersystem crossing. The actual values of the singlet excited-state lifetime are listed in Table 1 for **1-5**. After these decay processes, we observe a long-lived decay of several nanoseconds followed by an infinitely long decay most likely due to the triplet excited state.

Because both the ns and ps transient absorption spectra show broad positive absorption band from 500 nm to 800 nm, reverse saturable absorption is expected to occur for both ns and ps laser pulses in this spectral region. In our previously published work, we have demonstrated the reverse saturable absorption at 532 nm for ns pulses by nonlinear transmission measurement [28]. However, no quantitative information on the singlet and triplet excited-state absorption cross-sections was obtained. To obtain this important information for future photonic device applications, open-aperture Z-scan experiments are carried out using ns and ps pulses at 532 nm for **1-5**. The experimental data are then fitted by a five-level numerical model to abstract the singlet and triplet excited-state absorption cross-sections. The experimental and fitting results are shown in Figures 4, and the excited-state absorption cross-sections are listed in Table 2.

Figure 4 shows a typical Z-scan result for complex **2** at 532 nm. For both ns and ps Z scans, the transmission decreases when the sample solution is moved closer to the focal plane, which is a characteristic of reverse saturable absorption. By using the ground-state absorption cross-section (σ_g) obtained from the UV-Vis absorption spectrum, the triplet excited-state lifetime and quantum yield from the triplet transient difference absorption measurement, and the singlet excited-state lifetime obtained from the decay of the fs transient absorption as the input parameters, we have fitted the open-aperture Z-scan results using the five-level model. The fitting curve is displayed as a solid line in Figure 4, and the set of singlet and triplet excited-state absorption cross-sections that give rise to the best fitting results are provided in Table 2. The singlet excited-state absorption cross-section (σ_s) is obtained to be 28 ± 2 cm², and the triplet excited-state absorption cross-section (σ_T) is 12 ± 1 cm². This gives rise to a ratio of 26.2 for σ_s/σ_g and 11.2 for σ_T/σ_g . The Z-scan curves for the other four complexes are quite similar, and the resultant singlet and triplet excited-state absorption cross-sections are given in Table 2 as well. The results clearly show that the combination of ratios of σ_s/σ_g and σ_T/σ_g is much larger for **1**, **2** and **4** than those for **3** and **5**, which are consistent with the nonlinear transmission trend reported previously by our group for ns laser pulses at 532 nm. This indicates that critical parameter that determines the nonlinear transmission for a reverse saturable absorber is the ratio of the excited-state absorption cross-section to that of the ground-state absorption cross-section. For platinum complexes **1-5**, since the intersystem crossing times (given in Table 1) are of the similar magnitude as the pulsewidth of the ps laser (21 ps) used for the Z-scan measurements, both the singlet and triplet excited state contribute to the observed ps Z-scan signal, whereas the ns Z scan is dominated by the triplet excited state.

To evaluate whether these complexes could be potential broadband reverse saturable absorbers as their transient absorption spectra indicated, Z scans at different wavelengths for complex **1** were conducted. Complex **1** was selected for the wavelength-dispersion study because it is one of the strongest saturable absorbers at 532 nm among these five complexes. Because of the available laser sources, the wavelength dispersion Z scan was only performed using the ps laser. Reverse saturable absorption was observed from 500 to 600 nm for **1**. Because in ps scale, both the singlet and the triplet excited-state absorption contribute to the observed Z scan, and the triplet transient absorption at the wavelength range of 500 to 600 nm is pretty flat, it is reasonable to use the triplet excited-state absorption cross-section obtained from the fitting of the ns and ps Z-scan curves at 532 nm as the input parameter to fit the ps Z-scan curves at the other wavelengths. The resultant singlet excited-state absorption cross-sections are provided in Table 3. Although the σ_s does not show a drastic variation at different wavelengths, the ground-state absorption cross-section decreases significantly at longer wavelengths. As a result, the ratio of σ_s/σ_g increases two orders of magnitude from 500 nm to 600 nm. This indicates that stronger reverse saturable absorption would be observed at longer visible wavelengths.

4. Conclusion

The photophysical and Z-scan studies of the five 4'-(5'''-R-pyrimidyl)-2,2':6',2''-terpyridyl platinum(II) phenylacetylide complexes reveal that these complexes exhibit broadband singlet and triplet excited-state absorption from the visible to the near-IR region (500 – 800 nm). Therefore, reverse saturable absorption is observed at 532 nm for both ns and ps laser pulses for all these complexes. In addition, RSA is observed from 500 to 600 nm for **1** for ps laser pulses. Fitting of the experimental Z-scan data using a five-level dynamic model gives rise to the quantitative singlet and triplet excited-state absorption cross-sections, which varies from $(18\pm1)\times10^{-18}$ cm² to $(50\pm5)\times10^{-18}$ cm² for σ_s and $(11\pm1)\times10^{-18}$ cm² to $(14\pm2)\times10^{-18}$ cm² for σ_T at 532 nm, corresponding to a ratio of 6.5 – 29.8 for σ_s/σ_g and 2.8 – 11.2 for σ_T/σ_g for **1-5**. Complexes **1**, **2** and **4** exhibit a much larger σ_s/σ_g compared to those of **3** and **5**. Furthermore, the σ_s/σ_g ratio increases from 1.9 at 500 nm to 260 at 600 nm for complex **1**, indicating that this complex could exhibit much stronger reverse saturable absorption at longer visible wavelengths if measured using solutions with the same linear transmission at each respective wavelength.

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Table 1. Photophysical parameters of terpyridyl platinum complexes **1-5** in CH₃CN

	1	2	3	4	5
$\lambda_{\text{abs}}/\text{nm}^{\text{a}}$	463	436	456	463	470
$\lambda_{\text{S1-Sn}}/\text{nm}^{\text{a}}$	717	685	712	719	766
$\tau_{\text{s}}/\text{ps}^{\text{a}}$	37 ± 23	56 ± 17	139 ± 128	42 ± 8	46 ± 16
$\lambda_{\text{T1-Tn}}/\text{nm}^{\text{b}}$	725	720	755	730	785
$\tau_{\text{T}}/\text{ns}^{\text{b}}$	420	660	130	340	130
$\Phi_{\text{T}}^{\text{b}}$	0.65	0.53	0.19	0.64	0.66
$\tau_{\text{isc}}/\text{ps}^{\text{c}}$	57	106	732	66	70

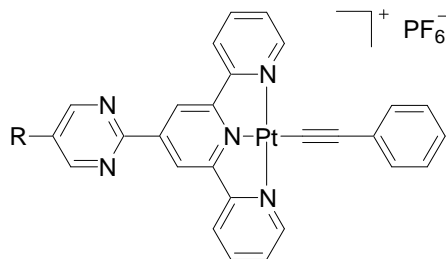
^a From this work. ^b From Ref. 28. ^c $\tau_{\text{isc}} = \tau_{\text{s}}/\Phi_{\text{T}}$

Table 2. Best-fit excited-state photophysical parameters of complexes **1-5** at 532 nm

	$\sigma_{\text{g}} / 10^{-18} \text{ cm}^2$	$\sigma_{\text{s}} / 10^{-18} \text{ cm}^2$	$\sigma_{\text{T}} / 10^{-18} \text{ cm}^2$	$\sigma_{\text{s}}/\sigma_{\text{g}}$	$\sigma_{\text{T}}/\sigma_{\text{g}}$
1	1.30	32±2	12±2	29.2	9.2
2	1.07	28±2	12±1	26.2	11.2
3	1.53	18 ± 1	14±2	11.8	9.2
4	1.68	50±5	11±1	29.8	6.5
5	4.59	30±2	13±1	6.5	2.8

Table 3. Best-fit singlet excited-state absorption cross section of complex **1** at various wavelengths

λ/nm	$\sigma_{\text{g}} / 10^{-18} \text{ cm}^2$	$\sigma_{\text{s}} / 10^{-18} \text{ cm}^2$	$\sigma_{\text{s}}/\sigma_{\text{g}}$
500	9.18	17.5±0.5	1.9
532	1.30	38±2	29.2
550	0.709	27 ± 1	38.1
570	0.302	15±2	49.7
600	0.096	25±2	260.4



R = H (**1**); OEt (**2**); Ph (**3**); Cl (**4**); CN (**5**)

Figure 1. Chemical structures of platinum complexes **1-5**

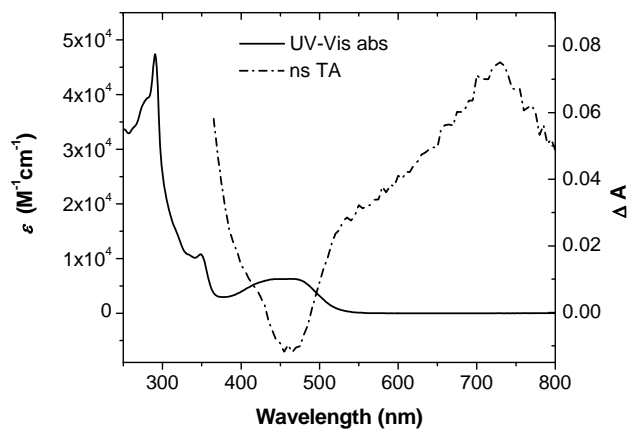


Figure 2. UV-Vis absorption spectra and ns transient difference absorption spectra of complex **4** in CH_3CN at zero time delay. $\lambda_{\text{ex}} = 355 \text{ nm}$.

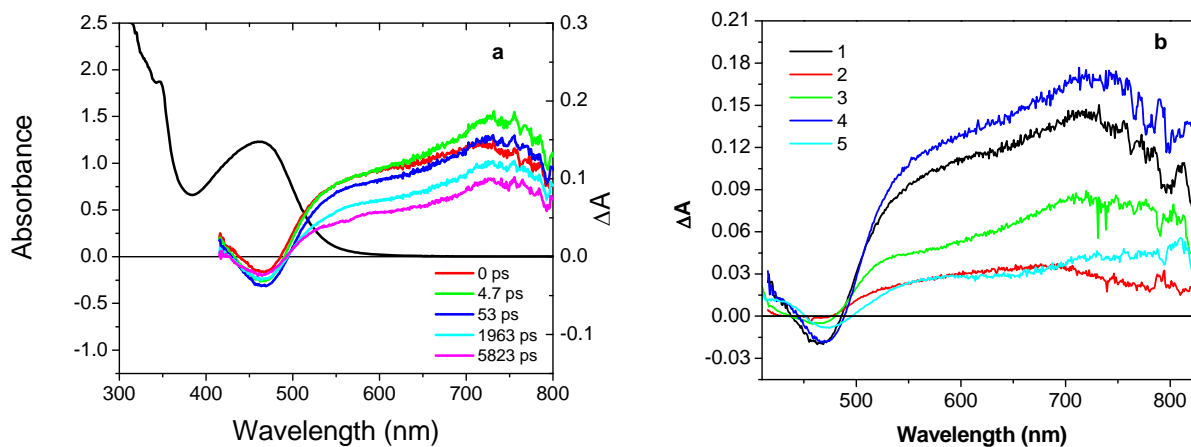


Figure 3. (a) Time-resolved fs transient difference absorption spectrum of **1** in CH_3CN . The black line is the UV-vis absorption spectrum of the CH_3CN solution of **1** used for the fs TA measurement. (b) fs transient difference absorption spectra of **1-5** at zero time delay after the excitation. $\lambda_{\text{ex}} = 400 \text{ nm}$.

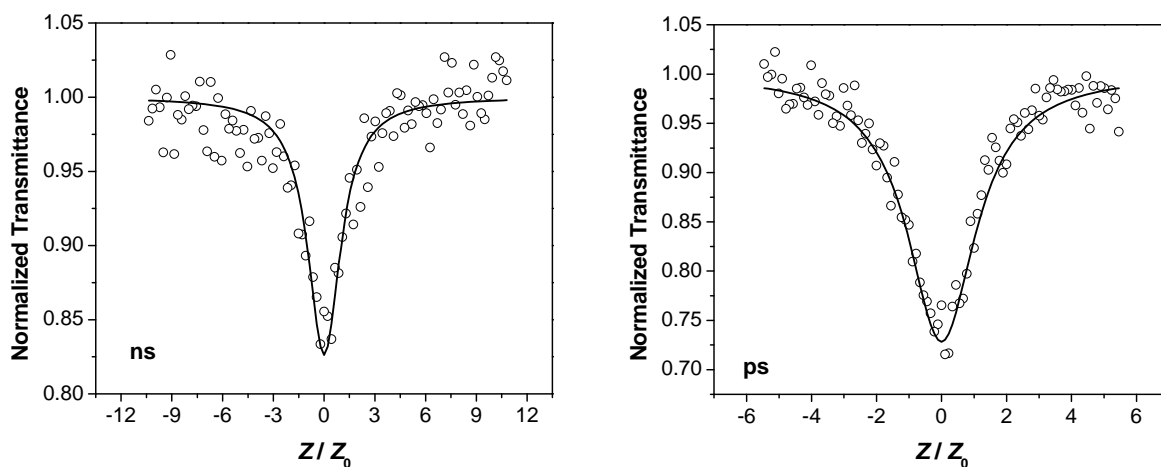


Figure 4. ns and ps open-aperture Z scans of complex **2** in CH₃CN at 532 nm. The concentration used for the ns Z-scan experiment was 2.9×10^{-3} mol/L, and 2.3×10^{-3} mol/L for the ps experiment. The energy used was $4.3 \mu\text{J}$ for ns measurement, and $2.7 \mu\text{J}$ for ps measurement. The open circle represents the experimental data, and the solid line indicates the theoretical fitting curve.

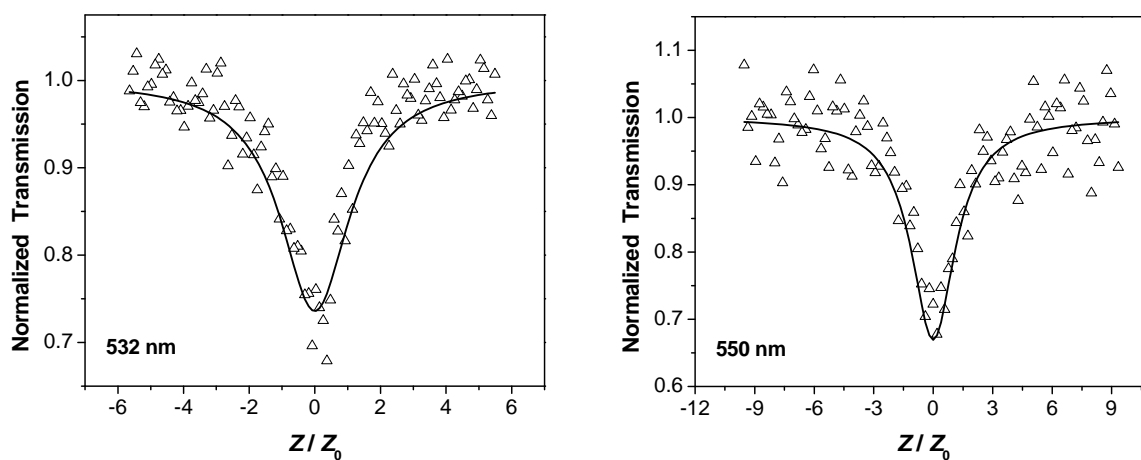


Figure 5. ps Z-scans of complex **1** in CH₃CN at 532 nm and 550 nm. The concentration used for measurement at 532 nm was 1.5×10^{-3} mol/L, and 3.3×10^{-3} mol/L at 550 nm. The energy of the laser used was $2.7 \mu\text{J}$ at 532 nm, and $2.4 \mu\text{J}$ at 550 nm.